

**MAGNETIC RESONANCE STUDY OF LIGAND RELAXATION
BEHAVIOUR IN SOME TRANSITION METAL COMPLEXES
IN SLOW MOTION LIMIT**

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of

MASTER OF PHILOSOPHY

By

PRADEEP KUMAR SRIVASTAVA

to the

**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
APRIL, 1980**

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"MAGNETIC RESONANCE STUDY OF LIGAND RELAXATION BEHAVIOUR
IN SOME TRANSITION METAL COMPLEX IN SLOW TUMBLING LIMIT"
submitted by Sri PRADEEP KUMAR SRIVASTAVA is a record of
bonafide research work carried out by him under my
supervision. The work embodied in this thesis has not
been submitted elsewhere for a degree.

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STATEMENT

I hereby declare that the matter embodied in this report is the result of investigations carried out by me in the Dept. of Chemistry, Indian Institute of Technology, Kanpur, under the supervision of Prof. P. Raghunathan.

In keeping with scientific tradition, wherever work done by others has been utilized, due acknowledgement has been made.

Pradeep Kumar Srivastava
Pradeep Kumar Srivastava

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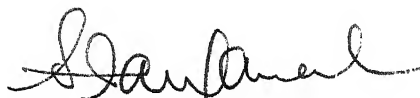
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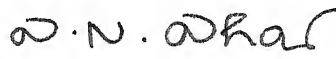
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This is to certify that Mr. Pradeep Kumar Srivastava has satisfactorily completed all the courses required for the M.Phil degree programme. These courses include:

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Chm 646 Bio-Inorganic Chemistry
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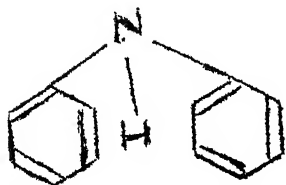
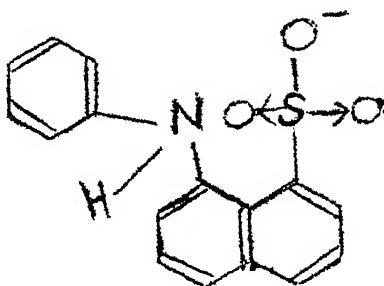
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INTRODUCTION

This project reports the synthesis of some novel transition metal ion complexes and envisages the application of magnetic resonance and relaxation techniques to these. For enabling us to interpret experimentally observable ^{13}C and ^1H nuclear spin relaxation times (T_1 and T_2) of the paramagnetic metal ion complexes in a variety of solvent environments, a rigorous theory becomes necessary. Such a theory should consider the nuclear electron hyperfine (dipolar plus Fermi contact) interaction controlling the nuclear relaxation not only in the usual "fast tumbling" or Redfield limit but also in the more interesting, relatively unexplored limit of "slow motion" which is primarily affected by electron spin relaxation process. In this latter limit the theory is beginning to become available only in last few years, and the major part of this project is, therefore, a survey of recent theory in this area and an analysis of the implications of the theory to studies of metal ion systems bound in different environments.

EXPERIMENTAL SECTION

The ligands used for complexation: 8 Anilino-1-naphthalene sulphonic acid (L_1) and N-diphenylamine (L_2) is used as such without purification.

Structure L_2 Structure L_1

(1) Preparation of tetrakis-N-diphenylamine cis-dioxygenal molybdenum(VI) $\left[\text{MoO}_2 (\text{C}_6\text{H}_5\text{-N-C}_6\text{H}_5)_4 \right]$ (A):

Took 1.5 g of N-diphenylamine, dissolved it in 50 ml of ethanol and added 10 ml of glacial acetic acid. To the above solution, added a solution of 1.0 g of sodium hepta-molybdate in 100 ml of water. A crystalline white complex precipitated immediately and was washed with ethanol; yield 90%.

(2) Preparation of bis-8-anilino-1-naphthalene-sulphonic acid cis-dioxygenal molybdenum(VI) $\left[\text{MoO}_2 (\text{C}_6\text{H}_5\text{-N-C}_{12}\text{H}_6\text{SO}_3)_2 \right]$ (B):

Took 1.0 g of sodium hepta-molybdate and dissolved it in 100 ml of water. To the above solution added 1.5 g 8-anilino-1-naphthalene sulphonic acid potassium salt dissolved in 50 ml of ethanol solution and then added 10 ml glacial acetic acid to it.

The colour of solution becomes reddish brown. The the solution was refluxed for 6 hours. After cooling brown precipitate is formed. Filtered the above precipitate and washed it with ethanol; yield 50%.

(3) Preparation of bis-8-anilino-1-naphthalene sulphonic acid copper(II) $\left[\text{Cu} \left(\text{C}_6\text{H}_5 - \underset{\text{H}}{\text{N}} - \text{C}_{12}\text{H}_6\text{SO}_3 \right)_2 \right] (\text{C}) :$

Took 1.0 g of the copper propionate, dissolved it in 20 ml of ethanol and to this solution added a solution of 1.5 g 8-anilino-1-naphthalene sulphonic acid potassium salt dissolved in 50 ml of ethanol. Refluxed the above mixture for 8 hours. Dark green liquid is obtained. Kept the above solution for crystallization in freeze for 24 hours. Dark green crystals of bis-8-anilino-1-naphthalene sulphonic acid Cu(II) is obtained. Washed the crystals with ethanol; yield 40%.

(4) Preparation of tetrakis-N-diphenylamine $\left[\text{Cu} \left(\text{C}_6\text{H}_5 - \underset{\text{H}}{\text{N}} - \text{C}_6\text{H}_5 \right)_4 \right] (\text{D}) :$

1 g of copper propionate was dissolved in 20 ml of ethanol and a solution of 1.5 g N-diphenylamine in 50 ml ethanol was added. The mixture was refluxed for 6 hours when a dark-blue solution was obtained. The solution was kept for crystallization in freeze. Dark blue crystals were obtained which were washed with ethanol; yield 50%.

CHARACTERIZATION OF COMPOUNDS BY INFRARED SPECTRA

Infrared spectra of the compounds have been recorded at PE-580 using CsI optics at higher concentration as shown in Fig. A, B, C and D. The results are summarized in TABLE.

TABLE

Compound	ν cis $\overset{\text{O}}{\parallel}\text{M}=\text{O}$ (cm^{-1})	ν M-O (cm^{-1})	ν M-N (cm^{-1})	ν M-N + ν M-O (cm^{-1})
A	900 and 930	580	300	-
B	900 and 920	540	335	-
C	-	-	495	330
D	-	-	440	370

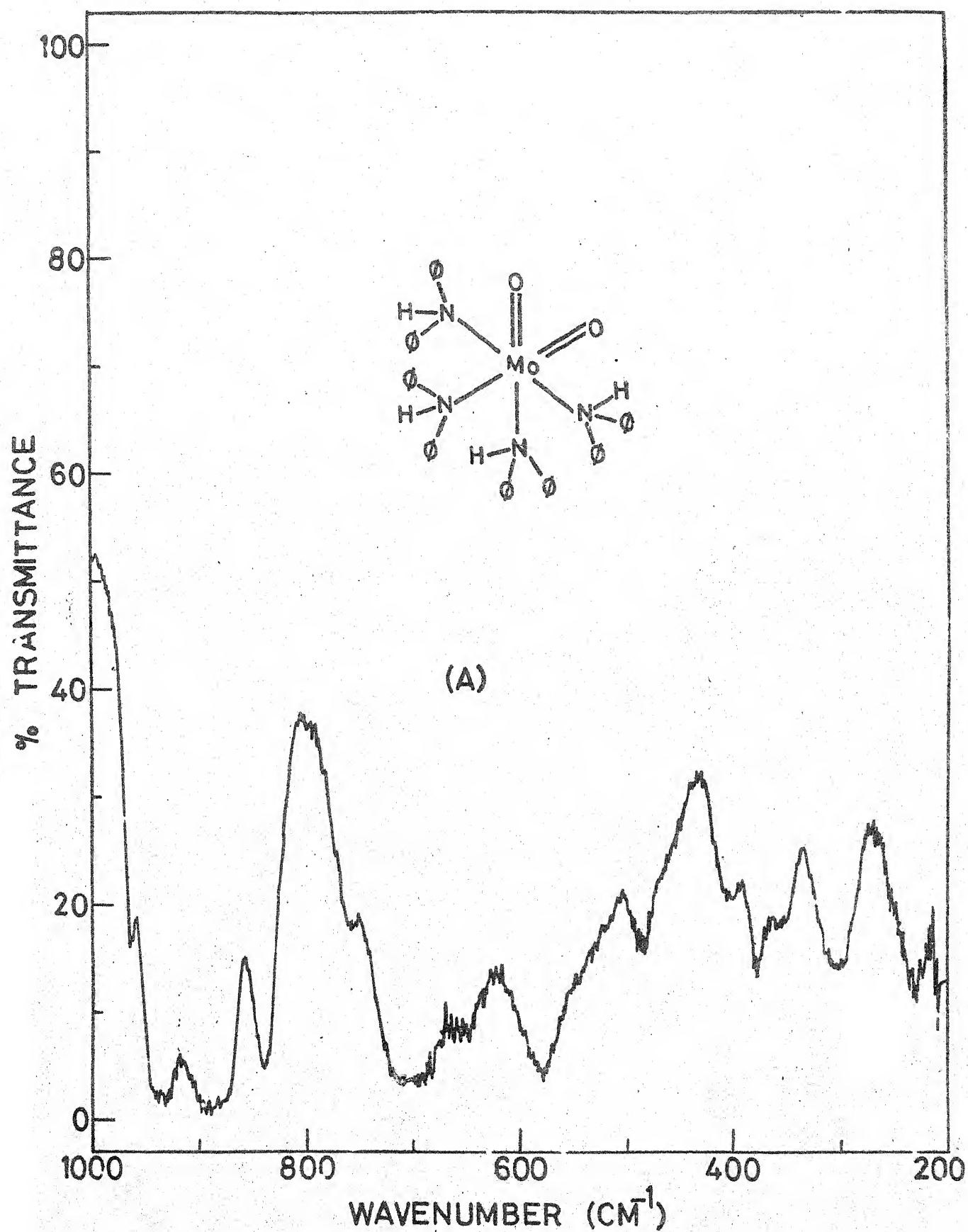


Fig. A. IR spectra of compound $\text{MoO}_2(\text{C}_6\text{H}_5\text{-NH-C}_6\text{H}_5)_4$ in CS_2 optics at higher concentration from 1000 cm^{-1} to 200 cm^{-1} ,

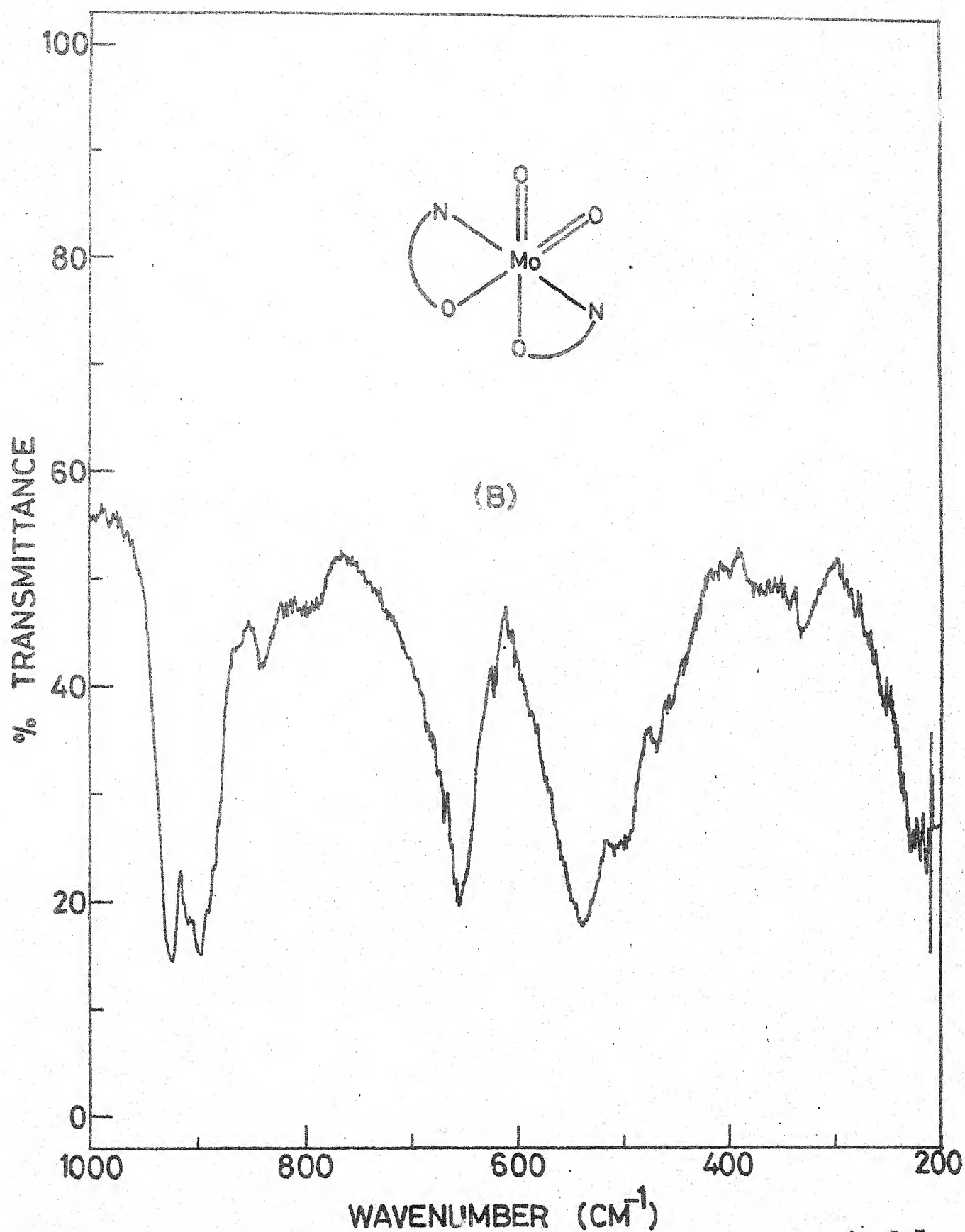
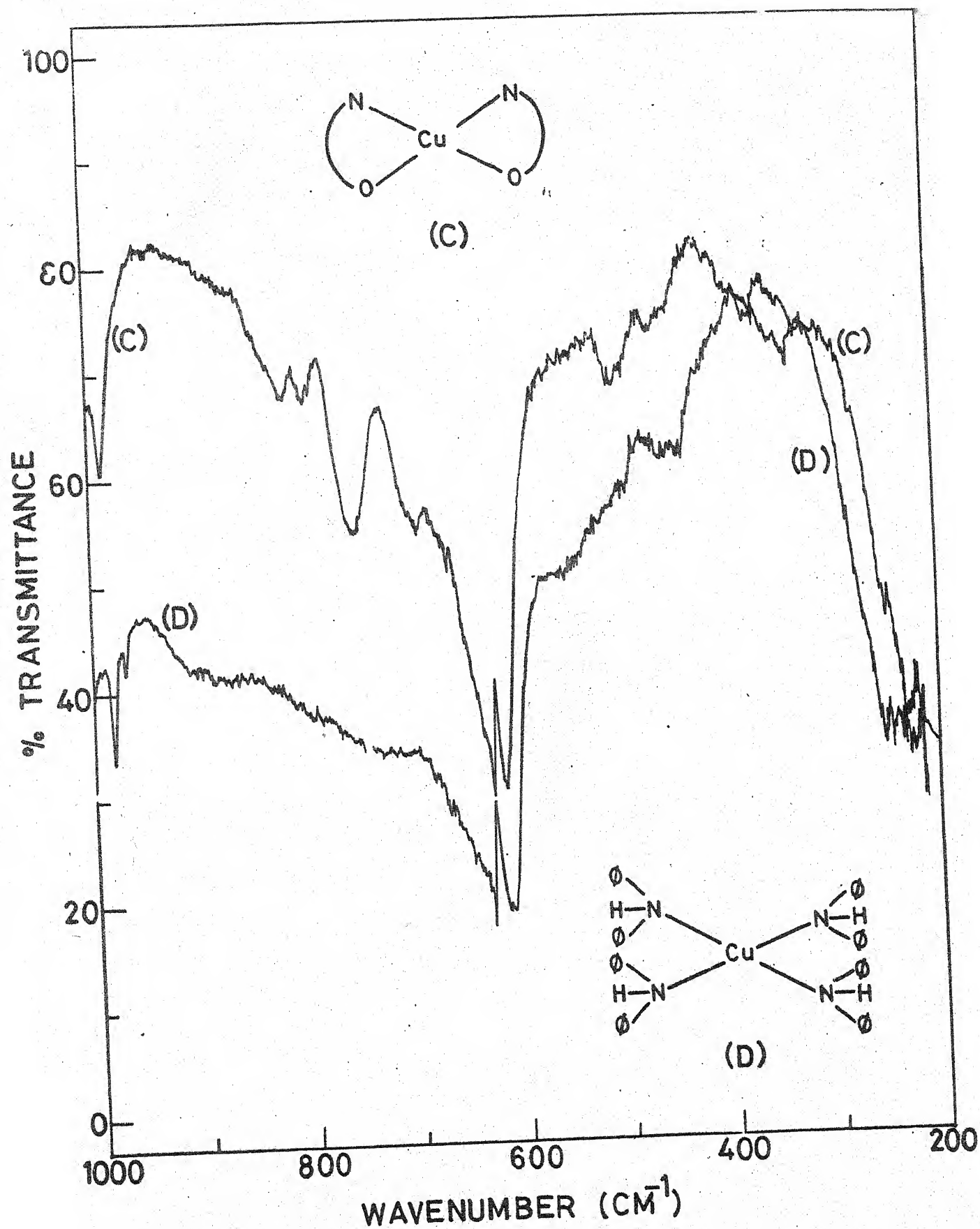


Fig. B. IR spectra of compound $\text{MoO}_2(\text{C}_6\text{H}_5\text{-N-C}_{12}\text{H}_6\text{SO}_3)_2$ in CsI optics at higher concentration from 1000 cm^{-1} to 200 cm^{-1} .

Fig. C. IR spectra of compound $\text{Cu}(\text{C}_6\text{H}_5-\underset{\text{H}}{\text{N}}-\text{C}_{12}\text{H}_6\text{SO}_3)_2$
in CsI optics at higher concentration from
 1000 cm^{-1} to 200 cm^{-1} .

Fig. D. IR spectra of compound $\text{Cu}(\text{C}_6\text{H}_5-\underset{\text{H}}{\text{N}}-\text{C}_6\text{H}_5)_4$
in CsI optics at higher concentration from
 1000 cm^{-1} to 200 cm^{-1} .



THEORY OF SPIN RELAXATION

There are two types of spin relaxations:

- (1) Nuclear spin relaxation, and
- (2) Electron spin relaxation.

1. Nuclear Spin Relaxation

There are two types of nuclear spin relaxation:

- (a) Spin-lattice or longitudinal relaxation characterized by a time T_1 .
- (b) Spin-spin or transverse relaxation, characterized by a time T_2 .

In general the nuclear spin relaxation of transition metal complexes is due to the following reasons:

i) The time modulation of direct dipole-dipole interaction, the Hamiltonian of dipolar coupling χ^{DD} being given by:^{1,2}

$$\chi^{DD}(t) = \gamma_I \gamma_S \hbar^2 \left[\frac{(\mathbf{I} \cdot \mathbf{S})}{r^3} - 3 \frac{(\mathbf{I} \cdot \mathbf{r})(\mathbf{S} \cdot \mathbf{r})}{r^5} \right] \quad \dots (1)$$

where \mathbf{r} is the radius vector for I to S and r is the distance between two moments.

ii) Fermi contact interaction between nuclear spin and electron spin, Hamiltonian for Fermi contact χ^{FC} is given by

$$\chi^{FC}(t) = a \mathbf{I} \cdot \mathbf{S}(t) \quad \dots (2)$$

where a = hyperfine interaction constant.

As the molecule rotates, r changes direction relative to the static magnetic field direction of the resonance experiment. The dipole-dipole interaction can then be written

$$\chi^{\text{DD}}(t) = \sum_{h=-2}^{h=+2} F_h(t) A_h(t) \quad \dots (3)$$

$F_h(t)$ contains the direction cosines of the electron nuclear radius vector at a time t .³

In the specific case of complexes containing an unpaired electron ($S = \frac{1}{2}$) the $A_h(t)$ term in Equation (3) is rendered time dependent due to rapid electron relaxation.

Because of the usual assumption that the time evolution of Equation (3) is a stationary random process¹ $F_h(t)$ becomes correlated with its value at a later time $(t + \tau)$ in terms of the expression:

$$\overline{F_h(t) F_h(t + \tau)^*} = \langle \overline{F_h^2(t)} \rangle \exp(-|\tau|/\tau_r) \quad \dots (4)$$

The left hand side of Equation (4) is usually called an auto-correlation function and its exponential decay has a characteristic time constant τ_r . (The horizontal bar on the left hand side of Eqn. (4) denotes ensemble averaging).

In the frequently encountered case of molecules in random motion in solution, τ_r becomes the rotational correlation time. In a similar way the spin tensor $A_h(t)$ can be characterized by

$$\overline{A_h(t) A_h(t+\tau)^*} = \langle \overline{A_h}^2(t) \rangle \exp(-|\tau|/T_e) \quad \dots(5)$$

Thus in Equation (5) electronic relaxation time T_e gets defined. Under the condition of electron spin relaxation process and nuclear reorientation process being uncoupled one can write a total auto-correlation function as the product of spatial and spin parts as given by³

$$\begin{aligned} \overline{\chi^{DD}(t) \chi^{DD}(t+\tau)^*} &= \sum \sum \overline{F_h(t) F_h(t+\tau)^*} \overline{A_h(t) A_h(t+\tau)^*} \\ &= \sum \sum \langle \overline{F_h}^2(t) \rangle \exp(-|\tau|/\tau_r) \langle \overline{A_h}^2(t) \rangle \exp(-|\tau|/T_e) \quad \dots(6) \end{aligned}$$

2. Electron Spin Relaxation in Paramagnetic Transition Metal Complexes

We shall now examine how the observable features of E.P.R. and N.M.R. experiments are affected in the presence of electron spin relaxation rates in paramagnetic transition metal complexes.

Case 1. E.P.R. Parameters

The effects here arise from the time modulation (due to molecular reorientation) of either the anisotropic parts of the g-tensor and electron nuclear hyperfine A-tensor and/or (for $S > \frac{1}{2}$) the quadratic zero field splitting. The principal time dependent processes are then governed by T_{1e} and T_{2e} ⁴ as given below:

$$\frac{1}{T_{1e}} = (g':g') \beta_e^2 H_o^2 \tau_R / 5 h^2 (1 + \omega_S^2 \tau_R^2) \quad \dots(7)$$

$$\frac{1}{T_{2e}} = \left[(g':g') \beta_e^2 H_o^2 R / 30 h^2 \right] \left[4 + 3 (1 + \omega_s^2 \tau_R^2)^{-1} \right] \dots (8)$$

Here $(g'; g')$ is the inner product of the anisotropic part of the g-tensor:

(1) We can explain the mechanism of electron spin relaxation and its dependence on the anisotropic "g" tensor⁴ in the following simple way:

In this mechanism the orbital energy eigen states of the crystal field Hamiltonian are mixed by the SPIN-ORBIT coupling such that the electron in the ground state has a non zero orbital angular momentum. Hence the mixing of eigen states alters the interaction with the magnetic field from a simple scalar interaction to a tensor interaction with a time dependent anisotropic "g" tensor. Through this SPIN-ORBIT interaction, the applied static field gives rise to fluctuating off diagonal matrix elements of the true spin in the laboratory frame as the molecule rotates which leads to Spin Relaxation.

(2) Another mechanism is the so called Van Vleck Rotational Process. In this mechanism the spin is relaxed by the SPIN-ORBIT coupling such that when spin state is changed the orbital state remains unchanged. For magnetic field induced Van Vleck relaxation the time dependent effective magnetic field is proportional to the average expectation value of $\langle L \rangle$:

$$H_{eff} = \xi \langle L \rangle / g \dots (9)$$

In the case of non-linear molecules $\langle L \rangle = 0$ and hence rotational

Van Vleck effect vanishes. Doddrell et al.⁵ have shown that in most experimental situations where H is applied $\langle L \rangle \neq 0$ and the rotational Van Vleck effect does occur. In effect the field induces a non-zero $\langle L \rangle$ which relaxes the spin through spin-orbit coupling.

The Van Vleck approach will be for more useful because the slowness of molecular rotation compared with the orbital relaxation of the molecules will be in orbital eigen states of $H_0 + \beta LH$. For H large, the matrices can be diagonalized exactly in the orbital reference frame and the value of $\langle L \rangle$ calculated exactly. The spin relaxation through $\xi \langle L \rangle S$, coupling can then be formed.

Since this mechanism is important only in certain solid state situations, we will not consider this further in our theory.

(3) Electron Spin Relaxation through a dynamic Jahn-Teller effect. Doddrell et al.⁵ have proposed that in solution dynamic Jahn-Teller forces account for the spin relaxation. This will apply for the ground state of molecules which interact asymmetrically with their electronic environment,

e.g., $Ti(II)$ (octahedral), low spin $Fe(III)$ (octahedral), low spin $Ru(II)$ (octahedral), but not in $Cu(II)$ square planar complexes.

If the Jahn-Teller forces are operative, the ground state potential energy surface has energy minima corresponding to distorted configurations of the complex. In the solid state, pseudo-rotations induced by lattice phonons occur with the

correlation time τ for such processes exhibiting a complex temperature variations T as given by Equation (10):

$$\frac{1}{\tau} = \frac{1}{\tau_0} \exp \left(- \frac{\Delta}{k_B T} \right) \quad \dots (10)$$

where Δ is the energy barrier between minima of the potential wells. This is based on the strain induced interactions⁶ whereby lattice phonons cause vibrational pseudo rotations (not applicable to solution) but J.T. effect is still operative in liquid state.

In this case the interactions are induced by a transfer of energy into the vibrational modes of freedom of the molecule resulting from the solute-solvent collisions. Thus solid state relaxation theory can be applied to such complexes in solution but the correlation time τ is likely to be related to the time between collisions.

If Δ is small τ is approximately the collision time 10^{-12} to 10^{-13} sec. For J.T. effected Octahedral Cu(II) systems the resulting electron spin relaxation time is given by:

$$\frac{1}{T_{1e}} = \frac{2}{3} \left(\frac{\Delta g}{g_{av}} \right)^2 \left(\lambda_x^2 \lambda_y^2 + \lambda_y^2 \lambda_z^2 + \lambda_z^2 \lambda_x^2 \right) \frac{1}{\tau} \quad \dots (11)$$

Δg is anisotropy in g tensor.

$$g_{av} = \frac{1}{3} \text{Trace}(g) \quad \dots (12)$$

λ_i where (i = x, y, z) the direction cosines of the static magnetic field.

This will apply to such ions in solutions except that the nuclear spin relaxation will be affected by an average electron spin relaxation time, the direction cosines being averaged by the rotational motion of the molecule.

This is valid only if $T_{1e} \gg \tau_r$ which is true for most of the paramagnetic transition metal complexes.

Case 2. Effects on Nuclear Magnetic Resonance Observables

In the presence of paramagnetic transition metal ion the observed Nuclear Magnetic Resonance line will be usually broadened and shifted. The amount of broadening and shifting will depend upon the respective contribution of dipolar-dipolar coupling and Fermi contact interaction to the nuclear relaxation (Equations (1) and (2)).

The nuclear spin lattice relaxation varies as γ_I^2 . Thus if the relaxation does not permit signal resolution with proton nuclear magnetic resonance, then the signal can be resolved by using nucleus of smaller γ_I such as ^{13}C or ^2H . ^{13}C resonance procedures have been successfully used^{7,8} and similarly for deuterium resonance.⁹ But the resolution enhancement does not occur in general corresponding to the theoretical value due to complication from the nuclear Overhauser effect¹⁰ which we will not discuss here, but in principle, Overhauser enhancement factors and ^1H , T_1

can be used to obtain τ_r .

THEORY OF SPIN RELAXATION IN "SLOW TUMBLING LIMIT" OF
TRANSITION METAL COMPLEXES

All earlier theories for the theoretical treatment of the electron spin relaxation are based on⁴ the assumption that tumbling times are too short i.e.,

$$\tau_r \ll T_{2e}$$

The best known among the theories is due to Redfield¹¹ which is essentially a density matrix approach.

The density matrix technique will not be detailed here and excellent references are available on the subject.^{12,13}

The advantage of this method is that we can in principle calculate properties of an ensemble in bulk without knowing the wavefunction. Particularly, the diagonal elements of the density matrix have a simple physical interpretation, the element ρ_{kk} is the probability that a randomly sampled member of the ensemble will be in state k, that is ρ_{kk} is the fractional population of state k.

Redfield density¹¹ matrix approach, for the theoretical treatment of electron spin relaxation is only valid provided

$$\tau_r \ll T_{2e}$$

... (13)

This limit is not applicable whenever nuclear magnetic resonance lines are sharp i.e., when

$$T_{2e} \leq \tau_r \quad \dots (14)$$

For example the condition given by Equation (13) is not applicable for nuclear relaxation in metallo proteins where $\tau_r > 10^{-8}$ s may be quite long.

In such cases we make the following approximations¹⁴
Doddrell et al.:

(i) A stochastic diffusion process is assumed in which each step is sufficiently small to give a very small fractional change in the density matrix. This allows the relaxation process to be described in terms of differential equation having the form of BLOCH-Equations.

(ii) Contribution to the correlation integral:

$$\int_0^t \overline{\chi(t) \chi(t+\tau)^*} d\tau \quad \dots (14)$$

for $\tau \gg \tau_r$ are negligible and thus the limit is changed from $0 \rightarrow \infty$ to $t, t_0 \rightarrow \infty$.

(iii) Contribution from higher order terms in the perturbation expansion may be neglected.

The above approximations are valid only when Equation(13) holds.

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For spin relaxation $S = 1/2$ in the Redfield limit the characteristic spin relaxation time $1/T$ is given by Eqn. (15):

$$\frac{1}{T} = \overline{\Omega_o}^2 \tau_c(t) / (1 + h^2 \omega^2 \tau_r^2) \quad \dots (15)$$

where Ω_o refers to the mean value of the dipolar interaction matrix in which the periodic part vanishes.

Applying Eqn. (15) to the specific case given by Slichter² in which the fluctuations are due to fluctuating magnetic field H which has no periodic component in the laboratory frame, we find

$$\overline{\Omega_o}^2 = \gamma^2 H^2$$

Relaxation will be induced by the two independent field components perpendicular to the direction of the initial alignment in the final reference frame. For T_2 the field component parallel to the static field directions will not have its periodicity transformed by the rotation of frame so $h = 0$ other component will be given by the periodicity of frequency ω by the frame rotation $h = 1$:

$$\frac{1}{T_2} = \gamma^2 \left\{ H_{zo}^2 \tau_r + \frac{H_{yo}^2 \tau_r}{(1 + \omega^2 \tau_r^2)} \right\} \quad \dots (16)$$

For T_1 in which $h = 1$ for both components.

$$\frac{1}{T_1} = \gamma^2 \left\{ \frac{H_{zo}^2 \tau_r}{(1 + \omega^2 \tau_r^2)} + \frac{H_{yo}^2 \tau_r}{(1 + \omega^2 \tau_r^2)} \right\} \quad \dots (17)$$

where z_0 and y_0 refer to the z and y axes in laboratory frame.

The total electron nuclear dipolar interaction time (τ_c)¹⁵ is given as

$$\frac{1}{\tau_c} = \frac{1}{T_{1e}} + \frac{1}{\tau_r} \quad \dots (18)$$

The appropriate expression for electron spin relaxation in the long correlation time or "Slow-Tumbling" limit have been recently derived by Doddrell et al.¹⁴

$$\frac{1}{T_{1e(I)}} = K J(\omega S) \quad \dots (19)$$

$$\frac{1}{T_{1e(II)}} = K J(2\omega S)$$

$$\frac{1}{T_{2e(I)}} = K [J(\omega S) + J(2\omega S)] \quad \dots (20)$$

$$\frac{1}{T_{2e(II)}} = K [J(0) + J(\omega S)]$$

where K is constant.

EFFECT OF VARIOUS DECAY MODES ON THE NUCLEAR SPECTRAL DENSITIES

The $J(\omega, T_e, \tau_r)$'s are a measure of the power available at angular frequency ω from the time dependent interaction and are just the Fourier transform of the autocorrelation function:¹

$$G(\tau, T_e, \tau_r)$$

$$\begin{aligned} J(\omega, T_e, \tau_r) &= \int_{-\infty}^{+\infty} G(\tau, T_e, \tau_r) \exp(i\omega t) d\tau \\ &= 2 \int_0^{\infty} G(\tau, T_e, \tau_r) \cos \omega t d\tau \end{aligned}$$

... (21)

The ratio of spectral densities of Gaussian decay and exponential decay is given by Equation (22):

$$\begin{aligned} \frac{J_{GE}}{J_{EE}} &= \left(\frac{1}{2\tau_r} \right) (T_e + \tau_r) \pi^{\frac{1}{2}} \exp(T_e^2 / 4\tau_r^2) \\ &\times (1 - \operatorname{erf}(\tau_c / 2\tau_r)) \end{aligned}$$

... (22)

From the above ratio to estimate the effects of two different decay processes have on the nuclear relaxation times through variations in the spectral density function for the following cases:

(i) if $T_e \ll \tau_r$

$$\frac{J_{GE}}{J_{EE}} = \frac{1}{2} \sqrt{\pi} = 0.87$$

In determining the nuclear relaxation time the actual value of T_e in two process should not differ significantly.

(ii) $T_e = \frac{1}{2} \tau_r \quad \frac{J_{GE}}{J_{EE}} = 1.02$

and the nuclear T_1 and T_2 values are not affected by the choice of spectral density.

$$(iii) T_e = \tau_r \frac{J_{GE}}{J_{EE}} = 1.14.$$

This choice is still not important in making the comparisons between J_{GE} and J_{EE} we assume that $\omega\tau \ll 1$. This is a good approximation that the T_{1e} dominates the nuclear T_1 and T_2 .

However, the choice of our limit over the Redfield limit could be important for nuclear spin relaxation in metallo proteins and/or at high magnetic field strengths.

The rotational correlation time for slow motion in transition metal complexes is derived by Doddrell et al.¹⁶

$$\tau_R = \tau_R^0 \exp (E_R/RT) \quad \dots (23)$$

τ_0 is constant, E_R is the activation energy for rotational reorientation where τ_0 is given by Eqn. (24):

$$\tau_0 = \left(\frac{2}{\pi} \right)^{-1/2} \frac{\Delta t}{m(\Delta\theta)^2} \quad \dots (24)$$

θ change in angular position due to reorientation

m = some fraction of $K_B T$ (K_B Boltzman constant, T is temp. $^\circ A$).

The activation energy obtained for N.M.R. relaxation time measurement is the barrier (in practice average) encountered by the solute molecule during a single angular step and thus it may be a useful parameter for solute-solvent interaction studies in future.

CONCLUDING REMARKS

In this work we have reported the preparation and characterization of four transition metal ion complexes and our future objective is to study the nuclear spin lattice (T_1) and spin-spin (T_2) relaxation time of the ligand structures by N.M.R. Spectroscopy. The theory which is necessary for our detailed study is presented in this report, and the complete set of N.M.R. measurements is hoped to be conducted in the near future.

E.S.R. SPECTRA

As a preliminary result, the e.s.r. spectrum at X-band has been recorded for the compound D.

$$g = 2.0036 \text{ for DPPH}$$

At room temperature from over modulated unresolved powder spectrum (Fig. E₂):

$$g_{\parallel} = 2.086 \text{ and } g_{\perp} = 2.219$$

This means that the g-tensor is axial, indicating axuality of the electron-nuclear interaction in the direction of the d_{z^2} orbital. At a much lower temperature (liquid N₂ 77°K) the e.s.r. obtained is shown in Fig. E₃.

This shows features of an orthorhombic g-tensor.

$$\begin{array}{ccc} \text{orthorhombic g-tensor} & \longrightarrow & \text{axial g-tensor} \\ (\text{low temperature}) & & (\text{room temperature}) \end{array}$$

This shows that there is a slow motion of the molecule in the solvent matrix.

We are examining the detailed lineshape changes in the light of the theory we have presented in this report.

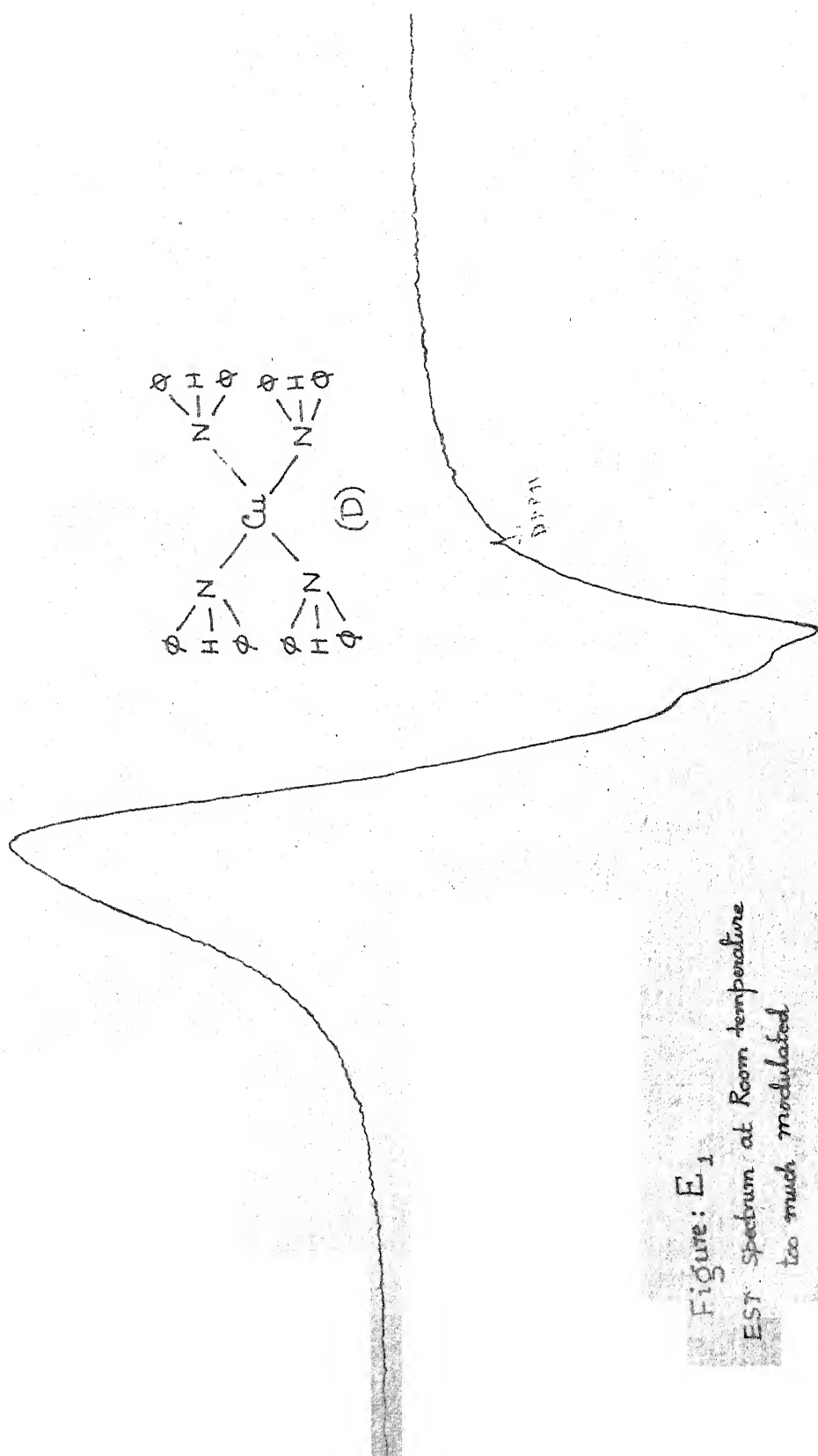
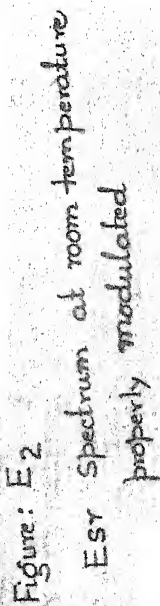


Figure: E₁
 ESR spectrum at Room temperature
 too much modulated



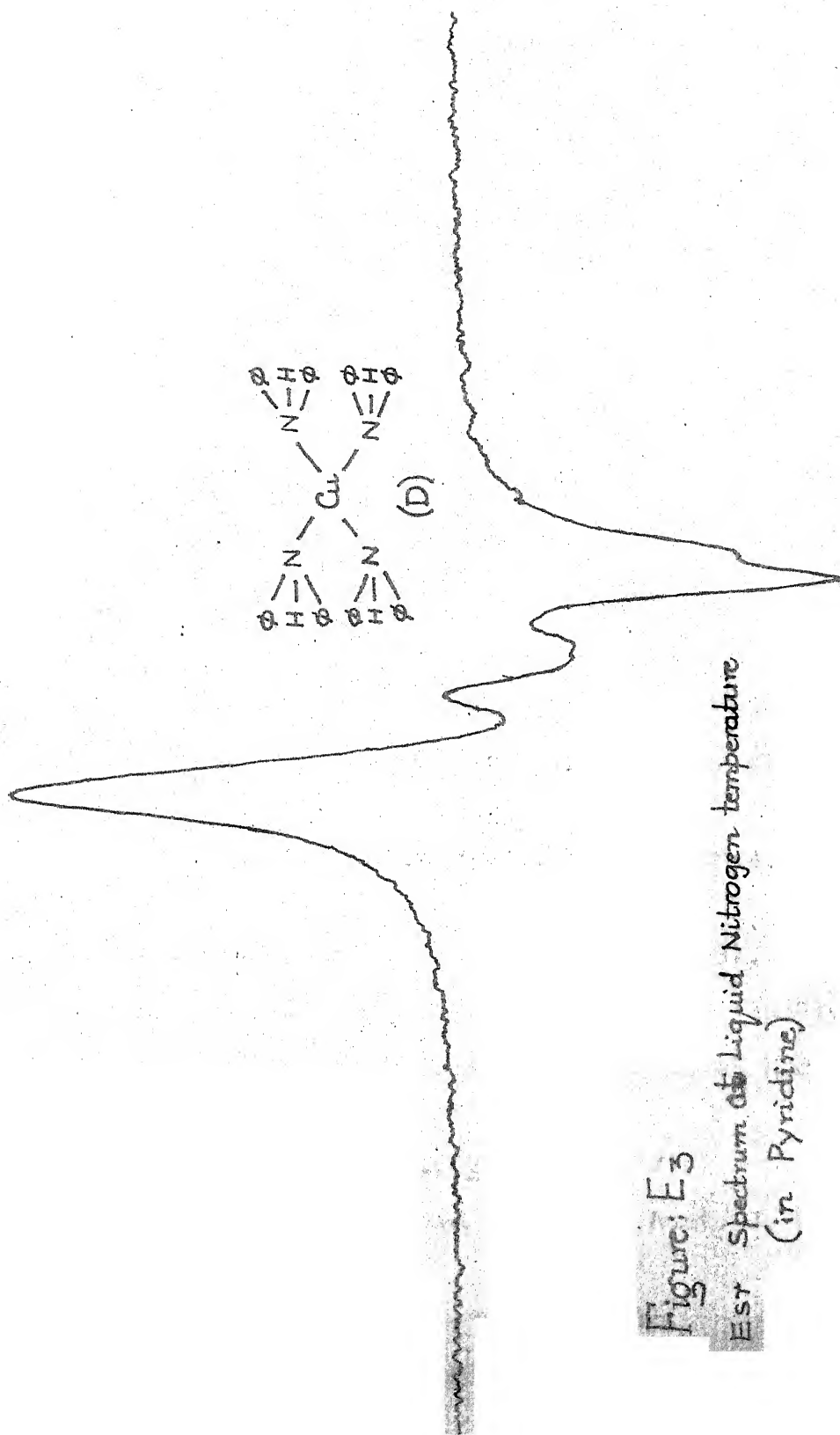


Figure: E3

ESR Spectrum at Liquid Nitrogen temperature
(in Pyridine)

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